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Determination of Rates of Reaction in the Gas-Phase in the
Troposphere. Theory and Practice. 1. Hierarchal Test Scheme

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DETERMINATION OF RATES OF REACTION
IN THE GAS-PHASE IN THE TROPOSPHERE

THEORY AND PRACTICE

1. Hierarchal Test Scheme

by

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Hierarchical Test Scheme

Contents	Page
Abstract	iii
A. Introduction	1
B. Theoretical Aspects	7
B.1. Direct Photoreaction	7
B.2. Indirect Photoreaction with Hydroxyl Radicals	9
B.3. Oxidation with Ozone	10
B.4. Net Photoreaction in the Troposphere	11
C. Screening Tests	11
C.1. Direct Photoreaction Involving a Laboratory Test and a Simple Assumption	11
C.2. Indirect Photoreaction with Hydroxyl Radicals Via Structure/Reactivity Relationships	13
C.3. Oxidation with Ozone Via Structure/Reactivity Relationships	15
D. Upper-Tier Laboratory Tests	16
D.1. Direct Photoreaction	16
D.2. Indirect Photoreaction with Hydroxyl Radicals	17
D.3. Oxidation with Ozone	18
E. References	19

Abstract

This publication represents the first in a series of reports on the theory and practice for determining rates of reaction in the gas-phase in the troposphere. Chemicals in the troposphere can undergo three principal transformation processes: (1) direct photoreaction which involves the absorption of sunlight, followed by transformation; (2) indirect photoreaction which involves the reaction of a chemical with hydroxyl radicals (OH); and (3) oxidation which involves the reaction of a chemical with ozone (O_3).

A quantitative measure of these three processes is given by the rate constants k_{dE} , k_{OH} , and k_{O_3} . The rate constant k_{dE} represents the first-order rate constant for direct photoreaction in the units of reciprocal time. The rate constants k_{OH} and k_{O_3} represent the second-order rate constants for the indirect photoreaction of a chemical with OH and oxidation with O_3 , respectively, in the units (concentration x time)⁻¹. The net transformation of a chemical in the gas-phase in the troposphere (k_{pE}) is then given by the sum of k_{dE} , $k_{OH}(OH)$, and $k_{O_3}(O_3)$, where the terms (OH) and (O_3) represent the hydroxyl radical and ozone concentrations in the troposphere, respectively.

A two-tiered hierarchal test scheme has been developed for determining the rate constants k_{dE} , k_{OH} , and k_{O_3} and estimating the half-lives [$t_{(1/2)E}$] for each of the transformation processes in the gas-phase in the troposphere. This test scheme is organized so that estimation techniques are used in screening

tests at the first level of testing followed by laboratory test methods in upper-tier tests. The screening tests give a rough estimate of the fate of a chemical in the gas-phase in the troposphere. Depending upon the results of these screening tests and the requirements in a risk assessment, upper-tier laboratory tests should be used to obtain more detailed and reliable information to determine the fate of a chemical in the gas-phase in the troposphere.

Subsequent reports will describe the theory and practice for: (1) estimating k_{OH} and k_{O_3} ; (2) measuring k_{dE} , k_{OH} , and k_{O_3} ; (3) estimating the half-life for each process; and (4) estimating the net half-life of a chemical in the gas-phase in the troposphere.

A. Introduction

Numerous chemicals enter the troposphere (i.e., the atmosphere surrounding the surface of the earth from 0 to 15 km where the temperature decreases with increasing altitude) from a variety of sources. For example, chemicals enter the troposphere as a result of burning of oil and coal, from the combustion of gasoline by a car, from the combustion of diesel oil by trucks, and from the release of volatile chemicals during manufacturing, processing, use, and disposal. Chemicals in the troposphere can undergo transformation by three principal transformation processes:

- (1) direct photoreaction which involves the absorption of light by a chemical, followed by transformation;
- (2) indirect photoreaction, which involves the reaction of a chemical with hydroxyl radicals (OH); and
- (3) oxidation, which involves the reaction of a chemical with ozone (O_3).

There is another transformation process involving the reaction of NO_3 radicals during the night which can transform a chemical. However, this transformation process only occurs for a few types of chemicals; hence, it will not be covered in this and subsequent reports.

A quantitative measure of the rate of these three processes is given by the rate constants k_{dE} , k_{OH} , and k_{O_3} . The rate constant k_{dE} represents the first-order rate constant for direct photoreaction in the units of reciprocal time (e.g.,

s^{-1} , h^{-1} , d^{-1}) . The rate constants k_{OH} and k_{O_3} represent second-order rate constants for the indirect photoreaction of a chemical with hydroxyl radicals and oxidation with ozone, respectively. The units of these two rate constants are concentration⁻¹ time⁻¹ (e.g., $cm^3 \text{ molecule}^{-1} s^{-1}$).

Figure 1 depicts a two-tiered hierarchal test scheme for determining the fate of a chemical in the troposphere. The first level of testing uses screening tests. For direct photoreaction, the screening test involves a simple assumption and a minimum of laboratory experimental data to estimate the rate of direct photoreaction. For indirect photoreaction with OH radicals and oxidation with O_3 , estimation methods are used which involve the application of structure/reactivity relationships to estimate k_{OH} and k_{O_3} . The second level of testing involves upper-tier tests which use laboratory procedures for determining k_{dE} , k_{OH} , and k_{O_3} .

This test scheme and the specific test methods were first proposed by Hendry and Kenley (1979) in a U.S. Environmental Protection Agency (USEPA) report to the Office of Toxic Substances (OTS). In the ensuing years, this test scheme and test methods were expanded and refined by

SRI International [Mill et al. (1982, 1982a, 1982b, 1983, 1985, 1987, 1988)]

Penn State University [Heicklen (1981)]

Figure 1. Hierarchal Test Scheme for Determining Rates of Transformation of a Chemical in the Troposphere

A. Direct Photoreaction

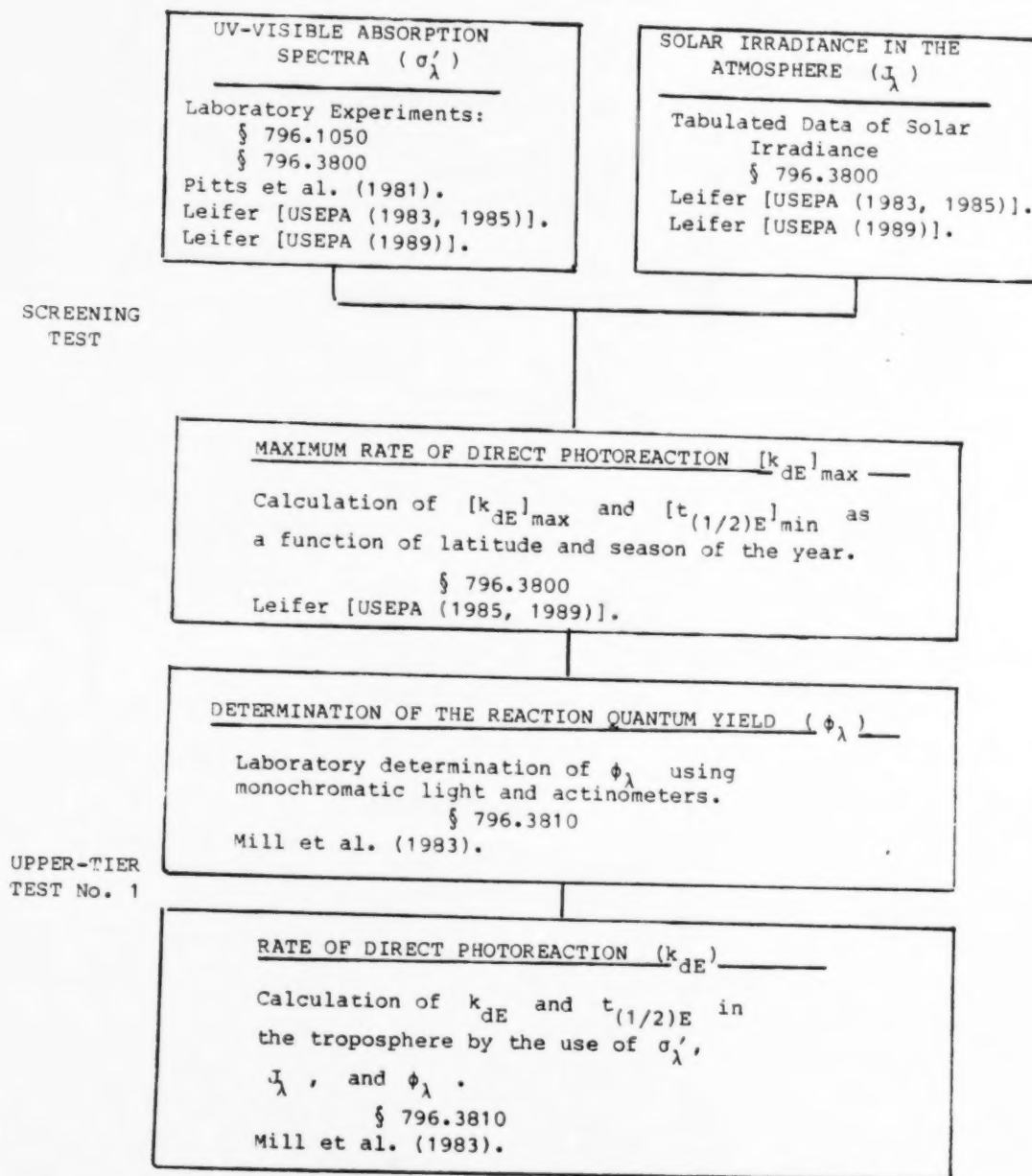


Figure 1. Continued

B. Indirect Photoreaction: Reaction with Hydroxyl Radicals

SCREENING
TESTS

RATE OF INDIRECT PHOTOREACTION (k_{OH})
Estimation Techniques:
Estimation of k_{OH} .
Atkinson (1986, 1986a, 1987, 1988).
§ 796.3900
Mill et al. (1982, 1982a, 1987).
GEMS:FAP; NEWFAP.
PCGEMS:PCFAP; PCNEWFAP.

CALCULATIONS
 $t_{(1/2)E}$ from k_{OH} and $[OH]_{av}$
in the troposphere.
§ 796.3900

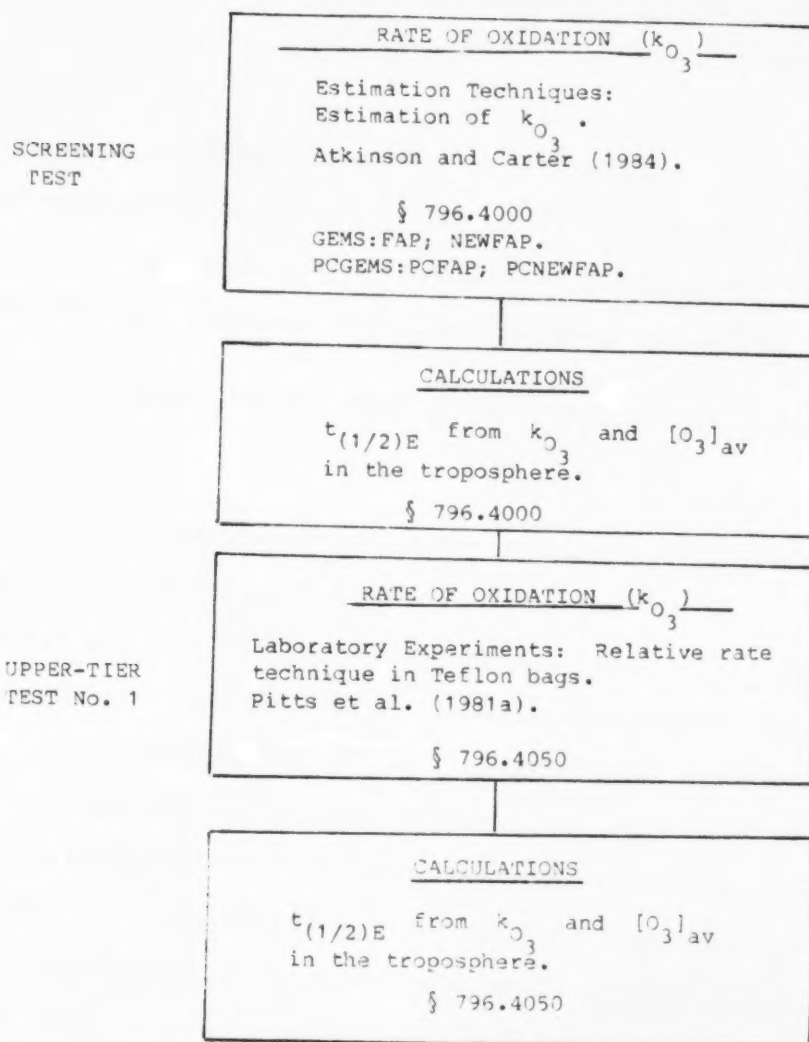
UPPER-TIER
TEST No. 1

RATE OF INDIRECT PHOTOREACTION (k_{OH})
Laboratory Experiments -- Relative rate
technique in Teflon bags.
§ 796.3950
Pitts et al. (1982).
Atkinson et al. (1981).

CALCULATIONS
 $t_{(1/2)E}$ from k_{OH} and $[OH]_{av}$ in
the troposphere.
§ 796.3950

Figure 1. Continued

C. Oxidation with Ozone



University of California/Riverside [Atkinson (1986, 1986a, 1987, 1987a, 1988, 1988a), Atkinson and Carter (1984), Atkinson et al., (1981), and Pitts et al. (1981, 1981a, 1982)]

for the Exposure Assessment Branch (EAB)/OTS/USEPA through OTS extramural funds and/or funds from the Office of Research and Development (ORD)/USEPA in support of OTS programs. In addition, this test scheme and test methods were expanded and refined by

Leifer [USEPA (1983, 1985, 1989, 1989a, 1989b)]

in EAB/OTS/USEPA.

A similar test scheme, which uses estimation methods at the screening level followed by laboratory test methods at the upper-tier level, have been evaluated by OECD (1987). The estimation methods, or structure/reactivity relationships, are those developed by SRI International (Mill) and University of California/Riverside (Atkinson). The laboratory methods evaluated involve absolute or relative rate measurements, some of which are those developed by SRI International. In 1988, OECD decided not to accept these test methods as test guidelines but published them in a "derestricted document" to be used as guidance to those who decide to carry out gas-phase transformations in the troposphere [see Atkinson, R. (1987a, 1988a) and Mill, Hendry, and Davenport (1987, 1988)].

B. Theoretical Aspects

B.1. Direct Photoreaction

Three parameters are essential for determining the direct photoreaction rate constant k_{dE} in the troposphere:

- (1) the absorption of sunlight by the chemical (cross section σ_λ or σ'_λ) ;
- (2) the overlap of the cross section with the actinic flux or solar irradiance J_λ ; and
- (3) the direct photoreaction quantum yield (ϕ_λ), the efficiency with which the absorbed light transforms the chemical into products.

In general, under environmental conditions, chemicals are present in the troposphere at very low concentrations. Under these conditions, the direct photoreaction rate constant k_{dE} is given by the mathematical relationship

$$k_{dE} = \sum_{\lambda} \phi_{\lambda} \sigma_{\lambda} J_{\lambda} \quad (1)$$

where σ_{λ} represents the cross section of a chemical in $\text{cm}^2 \text{ molecule}^{-1}$ at wavelength λ (nm); ϕ_{λ} is the direct reaction quantum yield at λ which is dimensionless; and J_{λ} is the solar irradiance in the troposphere at λ which is a function of latitude and season of the year. The wavelength λ corresponds to the wavelength centered over a specific wavelength interval $\Delta\lambda$ and λ covers the solar region from 290 nm to 800 nm. To obtain k_{dE} , the product of ϕ_{λ} , σ_{λ} , and J_{λ} (which is

$\phi_{\lambda} \sigma_{\lambda} J_{\lambda}$) is summed over all wavelengths where the chemical absorbs light from 290-800 nm (i.e., where σ_{λ} is non-zero).

The cross section σ_{λ} in gas-phase chemistry is defined by the Beer-Lambert law in the Napierian logarithm system. This definition, unfortunately, introduces considerable confusion in the literature since the cross section is measured spectroscopically in the decadic logarithm system. Thus, when measuring the cross section, a conversion factor must be used to obtain σ_{λ} . The cross section σ_{λ} in the Napierian logarithm system is equal to $2.303 \sigma'_{\lambda}$ where σ'_{λ} is the cross section in the decadic logarithm system which is measured by standard spectroscopic techniques [Test Guideline § 796.3800. Leifer [USEPA (1985)]] . The reaction quantum yield ϕ_{λ} can be determined by the method of Mill et al. (1983); and this method will be published as a future EPA Test Guideline § 796.3810.

The solar irradiance in the troposphere (J_{λ}) has been tabulated as a function of latitude (from 20°N. to 50°N. in 10° increments, from 0°N. to 70°N. in 10° increments, or from 10°N. to 50°N. in 20° increments) for the winter and summer solstices, the equinox, and for the averaged spring/summer and fall/winter seasons [Hendry and Kenley (1979); Hendry in Mill et al. (1982); Davenport (1985); Mill et al. (1985); and Leifer [USEPA (1983, 1985, 1989)]] . The J_{λ} values in these tables represent a 24-h averaged value in the units $\text{photons cm}^{-2} \text{ d}^{-1}$.

Since the direct photoreaction process is first-order, the half-life in the environment, $t_{(1/2)E}$, is given by the equation

$$t_{(1/2)E} = (0.693/k_{dE}) \quad (2)$$

$$t_{(1/2)E} = 0.693 / \sum \phi_{\lambda} \sigma_{\lambda} J_{\lambda} \quad (3)$$

where $t_{(1/2)E}$ is in the units of days.

B.2. Indirect Photoreaction with Hydroxyl Radicals

As a result of a series of complex reactions involving sunlight and chemicals present in the troposphere, a steady-state concentration of hydroxyl radicals is formed. These hydroxyl radicals (OH) are extremely reactive and can oxidize organic chemicals very easily. This process is called indirect photo-reaction, or photooxidation, and is just an oxidative process. The kinetics of the reaction of a chemical with hydroxyl radicals in the gas-phase in the troposphere, at a fixed temperature T, can be treated mathematically in the following manner:



$$-(dC/dt) = -k_{OH}C(OH) \quad (5)$$

where k_{OH} is the second-order rate constant in the units $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and C and (OH) represent the concentration of chemical and hydroxyl radicals, respectively. In the gas-phase, the chemical and hydroxyl radical concentrations are usually expressed in the units molecules cm^{-3} .

Since the chemical is present at very low concentrations in the troposphere at any given time, and a steady-state concentration of OH radicals is produced by sunlight, the hydroxyl radical concentration can be treated as a constant and

equation 5 becomes a pseudo first-order rate equation

$$-(dC/dt) = kC \quad (6)$$

where

$$k = k_{OH}(OH) \quad (7)$$

Since this transformation process is first-order, the half-life in the environment, $t_{(1/2)E}$, is given by the expression

$$t_{(1/2)E} = (0.693/k) = [0.693/k_{OH}(OH)] \quad (8)$$

It should be noted that (OH) represents the hydroxyl radical concentration which is a function of a number of variables. The best estimate of the global, seasonal, and diurnally averaged OH concentration in the northern hemisphere is 7.7×10^5 radicals cm^{-3} [Prinn et al. (1987)].

B.3. Oxidation with Ozone

As a result of a series of complex reactions involving sunlight and chemicals present in the troposphere, ozone is formed. Ozone is very reactive to certain classes of organic chemicals and can oxidize them very easily. This process is called photooxidation and is just an oxidative process. The kinetics of the reaction of a chemical with ozone in the gas-phase, at a fixed temperature T , can be treated mathematically in the following manner:



$$-(dC/dt) = k_{O_3} C(O_3) \quad (10)$$

where k_{O_3} is the second-order rate constant in the units $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and C and (O_3) represent the concentrations of chemical and ozone, respectively. The concentrations C and (O_3) are usually expressed in the units of molecules cm^{-3} .

Since the chemical concentration in the troposphere is very low at any given time t , so that in general the concentration of ozone is much greater than C , (O_3) can be treated as a constant. Therefore, using the same approach as described in Section B.2., it can be readily shown that

$$t_{(1/2)E} = [0.693/k_{O_3}(O_3)] \quad (11)$$

B.4. Net Photoreaction in the Troposphere

The net rate of transformation of a chemical in the troposphere is the sum of the rates of direct and indirect photoreaction and oxidation. The net rate constant k_{pE} in the troposphere is therefore given by the equation

$$k_{pE} = k_{dE} + k_{OH}(OH) + k_{O_3}(O_3) \quad (12)$$

and the net half-life in the troposphere is then

$$t_{(1/2)pE} = 0.693/k_{pE} \quad (13)$$

C. Screening Tests

C.1. Direct Photoreaction Involving a Laboratory Test and a Simple Assumption

The hierarchal test scheme for direct photoreaction is depicted in Figure 1.A. A simple screening test has been

developed using equation 1 {Test Guideline § 796.3800. Leifer [USEPA (1983, 1985, 1989)]}. As an approximation, it is assumed that the reaction quantum yield ϕ_λ is equal to 1, the maximum value. As a result, the upper limit for direct photoreaction in sunlight is obtained and equation 1 becomes

$$(k_{dE})_{\max} = \sum_{\lambda} \sigma_{\lambda} J_{\lambda} \quad (14)$$

But $\sigma_{\lambda} = 2.303 \sigma'_{\lambda}$ so that equation 14 becomes

$$(k_{dE})_{\max} = 2.303 \sum_{\lambda} \sigma'_{\lambda} J_{\lambda} \quad (15)$$

From equation 2, one obtains

$$[t_{(1/2)E}]_{\min} = [0.693 / (k_{dE})_{\max}] \quad (16)$$

and substituting equation 15 in 16 yields

$$[t_{(1/2)E}]_{\min} = 0.301 / \left(\sum_{\lambda} \sigma'_{\lambda} J_{\lambda} \right) \quad (17)$$

The maximum direct photoreaction rate constant can be estimated by combining the cross section σ'_{λ} of a chemical, measured in the laboratory by UV-visible absorption spectroscopy (Test Guideline § 796.3800), with the appropriate solar irradiance data J_{λ} . The values of J_{λ} have been tabulated from 10 to 50°N. latitude in 20° increments and from 20 to 50°N. latitude in 10° increments as a function of the summer and winter solstices and the equinox and for the averaged spring/summer and fall/winter seasons {Hendry and Kenley (1979); Hendry in Mill et al. (1982); Mill et al. (1985); and Leifer [USEPA (1983, 1985)]}. Tables of J_{λ} for 0°, 10°, 60°, and 70° N. latitude have been incorporated in a revised test guideline in a recent EPA report

{Leifer [USEPA (1989)]}. The products $\sigma'_\lambda J_\lambda$ are summed for all wavelengths λ from 290 to 800 nm where J'_λ is non-zero. This sum is $\sum_\lambda \sigma'_\lambda J_\lambda$. Substituting this sum in equation 15 yields $[k_{dE}]_{\max}$ and substituting this sum in equation 17 yields the minimum half-life $[t_{(1/2)E}]_{\min}$ in the environment.

This method of measuring $(k_{dE})_{\max}$ and $[t_{(1/2)E}]_{\min}$ has been revised and updated by Mill, Hendry, and Davenport (1987) in an OECD report in 1987. This test method has then been published by OECD in 1988 to be used as guidance to those who decide to carry out gas-phase transformations [Mill, Hendry, Davenport (1988)].

C.2. Indirect Photoreaction with Hydroxyl Radicals Via Structure/Reactivity Relationships

The hierarchal test scheme for indirect photoreaction with hydroxyl radicals is depicted in Figure 1.B. Structure/reactivity methods for estimating the second-order rate constant for the reaction of a chemical with hydroxyl radicals in the troposphere (k_{OH}) were proposed by Hendry and Kenley (1979) and by Hendry in Mill of SRI International (1982). These estimation methods were validated by Mill [Mill et al. (1982a)]. This work was supported by extramural funds from OTS and from funds from ORD, Eastern Regional Laboratory (ERL), Athens, GA, in support of OTS programs. These estimation methods were revised and updated by Mill, Hendry, and Davenport (1987) in an OECD report in 1987.

In parallel with the research work of SRI, OTS sponsored work with Heicklen of Penn State University, through a USEPA subcontract to Battelle, to review the research literature on

gas-phase transformations in the troposphere. As a result of this work, Heicklen developed structure/reactivity methods for estimating hydroxyl radical C-H abstraction rate constants from enthalpy data [Heicklen (1981)].

Based on the estimation methods developed by Hendry, Mill, and Heicklen, a computer program was developed by EAB/OTS to estimate k_{OH} for a variety of classes of organic chemicals in the gas-phase. This computer program is called GEMS:FAP or PCGEMS:PCFAP.

Other structure/reactivity methods for estimating the second-order rate constant for the reaction of a chemical with hydroxyl radicals in the troposphere (k_{OH}) have been developed by Atkinson [1986, 1986a, 1987, 1988]. The majority of the research by Atkinson and his coworkers, at the University of California/Riverside, was sponsored by the Office of Research and Development, Eastern Regional Laboratory (ERL), Research Triangle Park, NC, in support of EAB/OTS programs. These methods have been updated by Atkinson (1987a) in an OECD report in 1987. These methods were then published by OECD in 1988 to be used as guidance to those who decide to carry out the estimation of k_{OH} [Atkinson (1988a)]. These estimation methods will be used in the screening test.

All of the structure/reactivity methods developed to estimate k_{OH} are empirical and have been formulated solely on the basis of chemical structure. These structure/reactivity methods will be described in detail in a future EPA report and will be published as a generic EPA Test Guideline § 796.3900 to update

the screening test. The half-life of the chemical in the troposphere can then be calculated by substituting the estimated value of k_{OH} and the 24-hour averaged concentration of OH in the troposphere in equation 8. The FAP computer program will be updated and will use the structure/reactivity methods developed by Atkinson. The new computer program will probably be called GEMS:NEWFAP and PCGEMS:PCNEWFAP.

C.3. Oxidation with Ozone Via Structure/Reactivity Relationships

The hierarchal test scheme for indirect photoreaction with ozone is depicted in Figure 1.C. Structure/reactivity methods for estimating the second order rate constant for the reaction of a chemical with ozone in the troposphere (k_{O_3}) were proposed by Hendry and Kenley and by Hendry in Mill et al. (1982). This work was supported by extramural funds from OTS and funds from ORD/ERL, Athens, GA, in support of OTS programs. The structure/reactivity relationships were updated and revised by Mill, Hendry, and Davenport (1987) in an OECD report in 1987. These structure/reactivity relationships have then been published by OECD in 1988 to be used as guidance to those who decide to carry out the estimation of k_{O_3} [Mill, Hendry, and Davenport (1988)].

Based on the estimation methods developed by Hendry and Mill, a computer program was developed by EAB/OTS to estimate k_{O_3} for a variety of organic chemicals in the gas-phase. This computer program is called GEMS:FAP or PCGEMS:PCFAP.

Structure/reactivity methods for estimating the second-order rate constant for the reaction of a chemical with ozone in the troposphere (k_{O_3}) have also been developed by Atkinson and

Carter (1984). This work was also sponsored by the Office of Research and Development, ERL, Research Triangle Park, NC, in support of EAB/OTS programs.

All of the structure/reactivity methods developed are empirical and have been formulated solely on the basis of chemical structure. These structure/reactivity methods will be used in a screening test, to be described in a future EPA report, and will be published as a generic EPA Test Guideline \$ 796.4000. The half-life of the chemical in the troposphere can be calculated by substituting the estimated value of k_{O_3} and the 24-hour averaged ozone concentration (O_3) in the troposphere in equation 11. The FAP computer program will be updated and will use the structure/reactivity methods developed by Atkinson and Carter. The new computer program will be called GEMS:NEWFAP and PCGEMS:PCNEWFAP.

D. Upper-Tier Laboratory Tests

As a consequence of the results obtained in all three screening tests, only the dominant reaction pathway (or pathways) needs to be investigated in upper-tier laboratory tests. These upper-tier tests will be described in the following sections and are depicted for direct photoreaction, indirect photoreaction with hydroxyl radicals, and oxidation with ozone in Figures 1.A., B., and C., respectively.

D.1. Direct Photoreaction

For direct photoreaction, the reaction quantum yield ϕ_λ can be determined by irradiating a chemical and an actinometer in

the laboratory using monochromatic light at wavelength λ . The laboratory method of determining ϕ_λ is based on the work of SRI International, sponsored by EAB/OTS [Mill et al. (1983)]. The rate of photoreaction of the actinometer will give a measure of the irradiance of the light source at λ . The determination of ϕ_λ will be published as a future EPA Test Guideline § 796.3810. The reaction quantum yield ϕ_λ and the cross section σ'_λ , obtained by the use of the procedure in Test Guideline § 796.3800, can be combined with the solar irradiance J_λ to estimate k_{dE} and $t_{(1/2)E}$ as described in Section B.1. as a function of latitude and season of the year anywhere in continental United States. Tables of J_λ for 0°, 10°, 60°, and 70° N. latitude have been included in a recent EPA report to calculate k_{dE} in other parts of the United States (e.g., Alaska) [Leifer USEPA (1989)].

The methods of measuring ϕ_λ and σ'_λ , and estimating k_{dE} and the corresponding half-life $[t_{(1/2)E}]$ have been revised and updated by Mill, Hendry, and Davenport (1987) in an OECD report in 1987. These methods have then been published by OECD 1988 to be used as guidance to those who decide to carry out gas-phase transformation experiments [Mill, Hendry, and Davenport (1988)].

D.2. Indirect Photoreaction with Hydroxyl Radicals

The rate constant k_{OH} can be measured in the laboratory by using a relative rate technique in Teflon bags as proposed by Hendry [Hendry and Kenley (1979); and Hendry in Mill et al. (1982)] and developed by scientists at the University of

California/Riverside for EAB/OTS [Pitts et al. (1982); Atkinson et al. (1981)]. The relative rate technique involves the simultaneous reaction of a test chemical and a reference chemical with hydroxyl radicals (in large excess) in the gas-phase at 298 K and in air at a total pressure of 1 atmosphere and the measurement of the disappearance of test chemical and a reference chemical with time. From these data and the known value of the rate constant $[k_{OH}]_r$ of the reference chemical, k_{OH} for the test chemical can be determined. The half-life in the troposphere can be determined by substituting the measured value of k_{OH} in equation 8 along with the 24-hour averaged hydroxyl radical concentration (OH). This test method will be published as a future EPA Test Guideline § 796.3950.

D.3. Oxidation with Ozone

The rate constant k_{O_3} can be measured in the laboratory by using a relative rate technique in Teflon bags as proposed by Hendry [Hendry and Kenley (1979); and Hendry in Mill et al. (1982)] and developed by scientists at the University of California/Riverside for EAB/OTS [Pitts et al. (1981a)]. In this method, the relative rate technique involves the simultaneous reaction of a test chemical and a reference chemical with ozone (in large excess) in the gas-phase at 298 K in air at a total pressure of 1 atmosphere and the measurement of the disappearance of test chemical and reference chemical with time. From these data and the known rate constant $[k_{O_3}]_r$ for the reference chemical, k_{O_3} can be determined for the test chemical. The half-life in the troposphere can be determined by substituting

the measured value of k_{O_3} along with the 24-hour average ozone concentration in equation 11. This test method will be published as a future EPA Test Guideline § 796.4050.

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